

[Claim 2] A composition for aqueous paints as described in Claim 1 in which the emulsion containing fluorine (A) is obtained by copolymerizing the fluoroolefin in a range of 10 to 70 wt % and in which the emulsion containing an alkoxysilyl group (B) is obtained by copolymerizing the vinyl group containing alkoxysilyl groups in a range of 1 to 30 wt %.

[Claim 3] A composition for aqueous paints as described in Claims 1 and 2 in which the emulsion containing fluorine (A) and the emulsion containing alkoxysilyl groups (B) are obtained, respectively, by copolymerizing hydrophilic vinyl monomers having polyoxyethylene chains in a range of 0.1 to 10 wt %.

[Claim 4] A composition of aqueous paints as described in any one of Claims 1 through 3 characterized in that it contains a hardener.

[Detailed Description of the Invention]

[0001]

[Field of industrial use] This invention relates to various types of paints, for example, for building interior and exterior trim, automobiles, household electrical articles and plastics, and, in particular, to a composition for aqueous paints that is used for coatings requiring weather resistance and durability.

[0002]

[Prior art and problems the invention is intended to solve] In recent years, attempts have been made to change from the use of organic solvents to water-soluble or water-dispersible resins in the fields of paints and adhesive agents from the standpoints of providing countermeasures to pollution and of conservation of resources.

[0003] However, because conventional paints have cross-linking functional groups, they have the drawbacks that they are strongly affected by the surfactants that are used in polymerization, that the paint films that are formed exhibit markedly poor weather resistance, water resistance and contamination resistance and that the physical properties of the paint films are inferior to those of paints in which solvents are used.

[0004] For this reason, emulsions containing fluorine or emulsions containing alkoxysilyl groups have been proposed. However, there are the problems that water resistance is insufficient, that the stability of alkoxysilyl groups, which are readily hydrolyzed by water, is insufficient and that membrane forming capacity after long-term storage is decreased.

[0005]

[Means for solving the problems] The inventors conducted repeated and intensive research on the aforementioned problems. As a result, they perfected this invention by discovering that water resistance, durability and membrane forming capacity after long-term storage can be immensely improved by comparison to single emulsions by blending an emulsion containing fluorine and an emulsion containing alkoxysilyl groups.

[0006] Specifically, this invention is a composition for aqueous paints that is comprised of an emulsion containing fluorine (A) that is obtained by emulsion polymerization of a fluoroolefin and another vinyl monomer that can be copolymerized with it and an emulsion containing an alkoxysilyl group that is obtained by copolymerizing a vinyl monomer containing an alkoxysilyl group and another monomer that can be copolymerized with it.

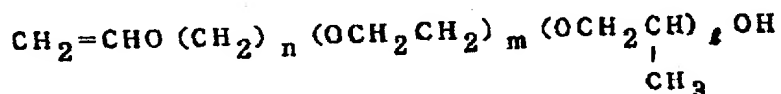
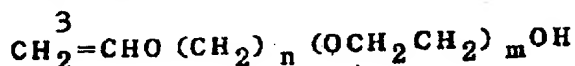
[0007] The fluoroolefins that are used in the manufacture of the emulsion containing fluorine include fluoroolefins in the strict sense of the term such as vinyl fluoride, vinylidene fluoride, tetrafluoroethylene, hexafluoropropylene, 1,1,3,3,3-pentafluoropropylene, 2,3,3,3-tetrafluoropropylene, 1,1,2-trifluoropropylene and 3,3,3-trifluoropropylene and fluoroolefins in the broad sense of the term including chlorotrifluoroethylene, bromotrifluoroethylene, 1-chloro-2,2-difluoroethylene or 1,1-dichloro-2,2-difluoroethylene as well as olefins having halogen atoms other than fluorine. The fluorine content of the polymer should be greater than 5% (wt %, the same hereafter).

[0008] The type of fluoroolefin and the copolymerization ratio should be selected from this standpoint. Copolymerization of the fluoroolefin so that it accounts for 10 to 70% of the total monomers is particularly desirable from the standpoints of weather resistance and durability.

[0009] Vinyl monomers that are copolymerizable with fluoroolefins include olefins such as ethylene and propylene, vinyl ethers such as ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether and cyclohexyl vinyl ether, vinyl esters such as butyl vinyl esters and octyl vinyl esters, vinyl compounds such as aromatic vinyl compounds of styrene and vinyl toluene, allyl ethers such as ethyl allyl ethers, allyl compounds including allyl esters such as butyl allyl esters, acryloyl compounds such as ethyl acrylate and methacryloyl compounds such as ethyl acrylate. In particular, olefins, vinyl ethers, vinyl esters, allyl ethers and allyl esters are used.

[0010] Mechanical stability can be improved without impairing the stability of the emulsion by copolymerizing hydrophilic vinyl monomers containing polyoxyethylene chains in emulsion (A), which contains fluorine. The stability of emulsion (B) containing mixed alkoxysilyl groups is better than that of other hydrophilic vinyl monomers.

[11] There are no particular limitations on the hydrophilic vinyl monomers having polyoxyethylene chains. For example, substances having the following structural formulas can be used.



(Wherein, n indicates 1 to 10, m indicates 1 to 30 and l indicates 1 to 30.)

[0012] The quantity of hydrophilic vinyl monomer having polyoxyethylene chains used should be 0.1 to 10%. When it is less than 0.1%, mechanical stability and the luster of the white enamel are decreased. When it exceeds 10%, the paint film becomes soft and is easily contaminated.

[0013] Emulsion polymerization can be performed by known methods. Specifically, it can be performed using surfactants and initiators.

[0014] There are no particular limitations on the surfactants. For example, they can be sulfonates such as sodium lauryl sulfonate, dodecylbenzene sodium sulfonate and isooctylbenzene sodium sulfonate, polyoxyethylene nonylphenyl ether sulfates such as Newcol-560SN and Newcol-560SF (manufactured by Nippon Nyukazai (Ltd.)) and Emal NC-35 and Reberu [phonetic]* WZ (manufactured by Kao (Ltd.)), polyoxyethylene allyl ether sulfates such as Newcol-707SF, Newcol-707SN, Newcol-723SF and Newcol-740SF, octylphenoxyethoxyethyl sulfates such as Newcol-861SE and polyoxyethylenetriodecyl sulfates such as Newcol-1305SN (manufactured by Nippon Nyukazai (Ltd.)).

[0015] Representative nonionic surfactants include polyoxyethylenes such as polyoxyethylene nonylphenyl ether and polyoxyethylene lauryl ether and silicones such as L-77, L-720, L-5410, L-7602 and L-7607 (manufactured by Union Carbide Company).

[0016] Use of a reactive surfactant having a polymerizable double bond in one molecule as a surfactant does not impair this invention. In particular, water resistance is improved when a reactive surfactant having a polyoxyethylene group in the molecule is used. Specific examples include Adecasorb [phonetic] NE-10, NE-20, NE-30, NE-40 and SE-10N (manufactured by Asahi Denka Kogyo (Ltd.)), Antox-MS-60 (manufactured by Nippon Nyukazai (Ltd.)) and Akuaron [phonetic] RN-20, RN-30, RN-50, HS-10, HS-20 and HS-1025 (manufactured by Dai-ichi Kogyo Seiyaku (Ltd.)).

* Translator's Note: Transliterated phonetically from the Japanese. As such, the spelling may differ from other transliterations.

[0017] These surfactants can be used individually or in combinations of 2 or more.

[0018] Water-soluble resins can be used in combination and polymerized. When this method is used, the water resistance of the paint film is improved.

[0019] The initiators that can be used include combinations of potassium persulfate, ammonium persulfate and acid sodium sulfite and Rongalit, combinations of acidic oxides such as t-butyl hydroperoxide, benzoyl peroxide, cumene hydroperoxide with p-menthane hydroperoxide, acid sodium sulfite and Rongalit. In order to obtain stable catalytic activity, a compound containing divalent iron ions such as iron sulfate and a chelating agent such as ethylenediaminetetracetic acid disodium salt may be used in combination.

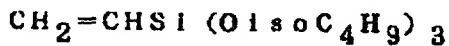
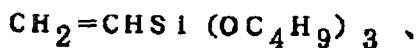
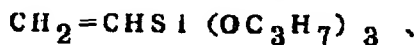
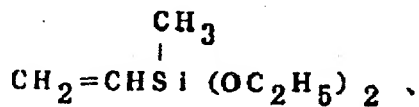
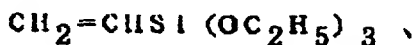
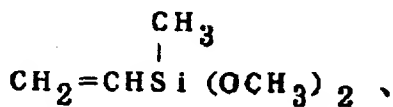
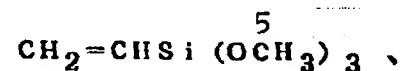
[0020] The quantity of initiator used is determined taking the total polymer weight as the standard and should be 0.01 to 10%, and, preferably, 0.05 to 5%.

[0021] Emulsion polymerization should ordinarily be performed at 0 to 100°C, and, preferably, 0 to 90°C and the reaction pressure should ordinarily be 1 to 100 kg/cm², and, preferably, at 2 to 50 kg/cm².

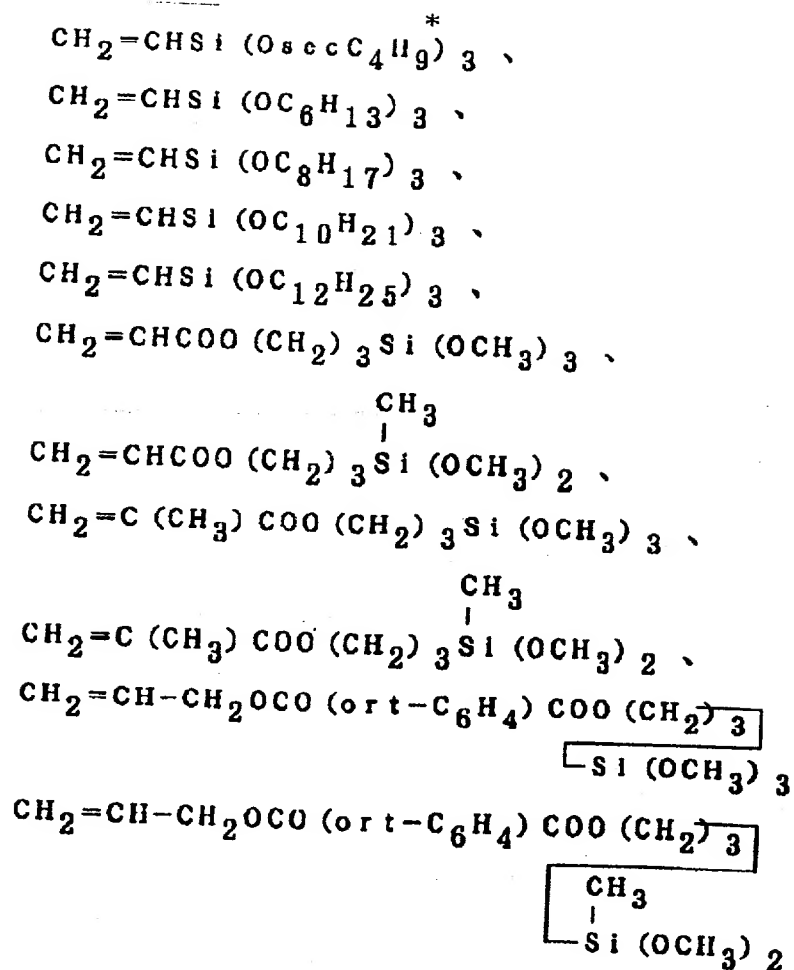
[0022] The concentration of solid matter in the emulsion should be 20 to 70%, and, preferably, 30 to 60%.

[0023] There are no particular limitations on the vinyl monomers having alkoxysilyl groups that are used in the manufacture of emulsion (B) having alkoxysilyl groups. Specific examples that can be cited are as follows.

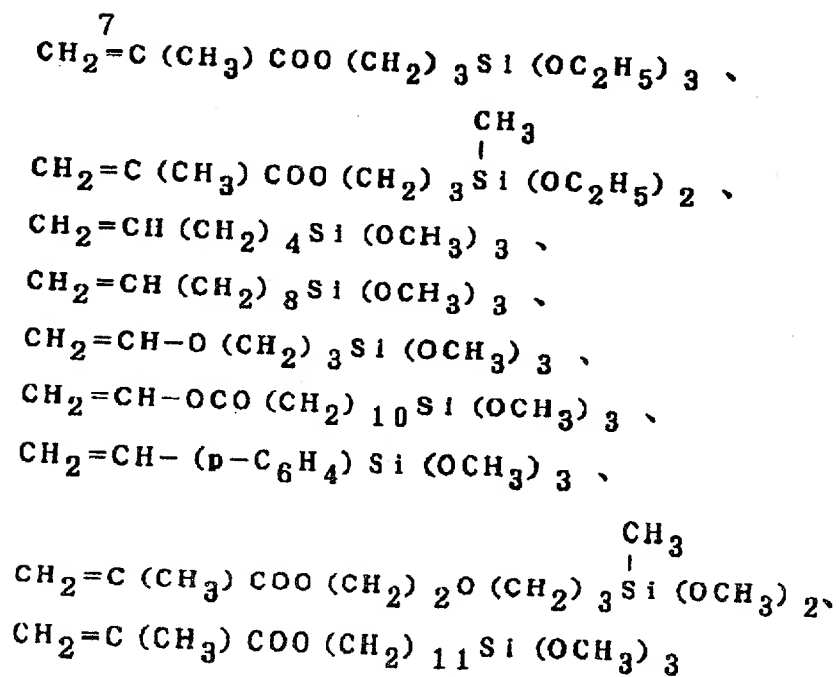
[Chemical Formula 2]



[Chemical Formula 3]



[Chemical Formula 4]



[0024] The monomers having alkoxysilyl groups may be used individually or in combinations of two or more.

[0025] The copolymerization ratio of vinyl monomer having alkoxysilyl groups should be 1 to 30%, and, preferably, 2 to 20%, of the total monomer. When it is less than 1%, there is a tendency for water resistance and weather resistance to deteriorate. When it exceeds 30%, the stability of the emulsion decreases.

[0026] There are no limitations on the other vinyl monomer that is copolymerizable with the vinyl monomer having an alkoxysilyl group. They can be, for example, acrylate or methacrylate monomers such as methyl acrylate or methacrylate, ethyl acrylate or methacrylate, butyl acrylate or methacrylate, isobutyl acrylate or methacrylate, benzyl acrylate or methacrylate and cyclohexyl acrylate or methacrylate, vinyl monomers containing fluorine such as triflyoroethyl acrylate or methacrylate, pentafluoropropyl acrylate or methacrylate, perfluorocyclohexyl acrylate or methacrylate, 2,2,3,3-tetrafluoropropylmethacrylate and β -(perfluorooctyl) ethyl acrylate or methacrylate, aromatic hydrocarbon vinyl monomers such as styrene, α -methylstyrene, chlorostyrene, 4-hydroxystyrene and vinyltoluene, α , β -ethylenic unsaturated carboxylic acids such as acrylic acid, methacrylic acid, malonic acid, maleic anhydride, itaconic acid, itaconic anhydride, crotonic acid, fumaric acid and sitolaconic [phonetic] acid, acids having polymerizable carbon-carbon double bonds such as styrene sulfonic acids and vinyl sulfonic acids or salts thereof (alkali metal salts, ammonium salts, amine salts, etc.), anhydrides such as maleic anhydride or half esters thereof with straight chain or branched alcohols having 1 to 20 carbon atoms, acrylates or methacrylates having amine groups such as dimethylaminoethyl acrylate or methacrylate, dimethylaminopropyl acrylate or methacrylate and diethylaminoethyl acrylate or methacrylate, acrylamide or methacrylamide, α -ethyl acrylamide or methacrylamide, N-butoxymethyl acrylamide or methacrylamide, N,N-dimethylacrylamide, N-methylacrylamide and acryloyl morpholine or hydrochlorides or acetates thereof, vinyl ester or allyl compounds such as vinyl acetate, vinyl propionate and diallyl phthalate, vinyl monomers having nitrile groups such as acrylonitrile and methacrylonitrile, vinyl monomers having epoxy groups such as glycidyl acrylate or methacrylate, vinyl monomers having hydroxyl groups such as 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 2-hydroxyethylvinyl ether, N-methylol acrylate or methacrylate, hydroxystyrene, Aronix [phonetic] 5700 (manufactured by Toa Synthetic Chemicals, Ltd.), Placel FA-1, Placel FA-4, Placel FM-1 and Placel FM-4 (manufactured by Daisel Chemicals, Ltd.), HE-10, HE-20, HP-10 and HP-20 (manufactured by Nippon Shokubai Kagaku, Ltd.), Brenma PP series, Brenma PEP series, Brenma AP-400, Brenma NKH-5050 and Brenma GLM (manufactured by Nippon Oils and Fats, Ltd.) and vinyl modified hydroxyalkyl vinyl monomers having hydroxyl groups, vinyl compounds which are condensation products of hydroxyalkyl esters of α , β -ethylenic unsaturated carboxylic acids such as hydroxyalkyl esters of acrylic acid or methacrylic acid and phosphoric acid or phosphoric acid esters or vinyl compounds such as acrylates or methacrylates that contain urethane bonds or siloxane bonds, compounds such as AS-6, AN-6, AA-6, AB-6 and AK-5 which are macromonomers manufactured by Toa Synthetic Chemicals (Ltd.), other monomers such as vinyl methyl ether, vinyl chloride, vinylidene chloride, chloroprene, propylene, butadiene, N-vinyl imidazole and vinyl sulfonic acid, polymeric photostabilizers such as LA87, LA82 and LA22 manufactured by Asahi Denka Kogyo (Ltd.) and polymeric ultraviolet ray absorbents.

[0027] In particular, the stability of the hydrolyzable silyl groups can be improved when these substances contain 60% or more of alkyl methacrylates having alkyl groups with 4 or more carbon atoms and cycloalkyl methacrylates having cycloalkyl groups with 4 or more carbon atoms. N-Butyl methacrylate and cyclohexyl methacrylate are particularly desirable from the standpoints of weather resistance, the glass transition temperature (T_g) of the emulsion resin, simplicity of preparation and price.

[0028] Further, water repellency, water resistance and durability are improved by using a vinyl monomer containing fluorine and a vinyl monomer containing siloxane.

[0029] In addition, the polymer that is produced can be made to have a cross-linking structure by using a monomer having two or more polymerizable unsaturated bonds such as, for example, polyethylene glycol dimethacrylate, ethylene glycol dimethacrylate or triallyl cyanurate.

[0030] Mechanical stability can be improved without decreasing the stability of the alkoxysilyl group by copolymerizing a hydrophilic vinyl monomer having a polyoxyethylene chain in the emulsion (B) having alkoxysilyl groups. Further, compositions for aqueous paints exhibiting good stability of the alkoxysilyl groups, no decrease in film forming capacity after long-term storage and good mechanical stability can be obtained by combining emulsion (A) containing fluorine in which a hydrophilic vinyl monomer having a polyoxyethylene chain has been copolymerized and also by using other hydrophilic monomers.

[0031] There are no particular limitations on the hydrophilic vinyl monomer having a polyoxyethylene chain. However, acrylic acid esters or methacrylic acid esters having polyoxyethylene chains are desirable. Specific examples that can be cited include Brenma PE-90, PE-200, PE-350, PME-100, PME-200, PME-400 and AE-350 (manufactured by Nippon Oils and Fats, Ltd.) and MA-30, MA-50, MA-100, MA-150, RA-1120, RA-2614, RMA-564, RMA-568, RNA-1114 and MPGL30-MA (manufactured by Nippon Nyukazai, Ltd.).

[0032] There should be 2 to 30 oxyethylene units in the polyoxyethylene chain. When there are less than 2, the mechanical stability and white enamel luster of the emulsion is inferior. When there are more than 30, the paint film softens and is easily contaminated.

[0033] The quantity of hydrophilic vinyl monomer having polyoxyethylene chains that is used should be 0.1 to 10%. When it is less than 0.1%, there is low mechanical stability and white enamel luster. When it exceeds 10%, the paint film softens and is easily contaminated.

[0034] Next, we shall describe the manufacture of the emulsified polymer (emulsion).

[0035] The emulsion polymerization methods that can be used include various emulsion polymerization methods such as the batch polymerization method, the monomer drip polymerization method and the emulsified monomer drip polymerization method. The monomer drip polymerization method and the emulsified monomer drip polymerization method are particularly desirable in terms of assuring stability during manufacture.

[0036] The hydrolyzable silyl groups can be stabilized by using an anionic surfactant having a polyoxyethylene chain as the surfactant that is used in the aforementioned manufacturing methods. Specific examples of anionic surfactants include polyoxyethylene nonylphenyl ether sulfates such as Newcol-560SN and Newcol-560SF (manufactured by Nippon Nyukazai, Ltd.) and Emal NC-35 and Reberu WZ (manufactured by Kao, Ltd.), polyoxyethylene allyl ether sulfates such as Newcol 707SF, Newcol 707SN, Newcol 723SF and Newcol 740SF, octyl phenoxyethyl sulfates such as Newcol 861SE and polyoxyethylene tridecyl ether sulfates such as Newcol 1305SN (manufactured by Nippon Nyukazai, Ltd.).

[0037] From the standpoints of polymerization stability and the stability of the hydrolyzable silyl groups, there should be 1 to 50 oxyethylene units in the polyoxyethylene chain. From the standpoint of the water resistance of the paint film obtained from the emulsion, anionic surfactants comprised of ammonium salts are desirable.

[0038] The anionic surfactant having a polyoxyethylene chain can be used in combination with other ionic surfactants or nonionic surfactants.

[0039] There are no particular limitations on the other ionic surfactants. For example, they can include such sulfonates as sodium lauryl sulfonate, dodecylbenzene sodium sulfonate and isooctylbenzene sodium sulfonate.

[0040] Representative nonionic surfactants include such nonionic surfactants as polyoxyethylenes such as oxyethylene nonylphenyl ether and polyoxyethylene lauryl ether and silicones such as L-77, L-720, L-5410, L-7602 and L-7607 (manufactured by the Union Carbide Company).

[0041] Use of reactive surfactants having a polymerizable double bond in one molecule as the surfactant does not impair this invention. In particular, water resistance is improved when a reactive surfactant having a polyoxyethylene group in the molecule is used. Specific examples that can be cited include Adekasorb NE-10, NE-20, NE-30, NE-40 and SE-10N (manufactured by Asahi Denka Kogyo, Ltd.), Antox MS-60 (manufactured by Nippon Nyukazai, Ltd.) and Akuaron RN-20, RN-30, RN-50, HS-10, HS-20 and HS-1025 (manufactured by Dai-Ichi Kogyo Seiyaku, Ltd.).

[0042] The quantity of anionic surfactant having polyoxyethylene chains that is used should be 0.01 to 20%, and, preferably, 0.05 to 10%, taking the total monomer weight as the standard. When it is less than 0.01%, polymerization becomes unstable. When it exceeds 20%, water resistance decreases.

[0043] Polymerization can be performed using a water-soluble resin in combination. When this method is used, the water resistance of the paint film is increased. Water resistance can be further increased by introducing an alkoxysilyl group into the water-soluble resin.

[0044] In order to perform polymerization in a more stable manner, it can be performed using a redox catalyst at a temperature less than 70°C, and, preferably, at a temperature of 40 to 65°C. For the purpose of silyl group stabilization, the pH during polymerization should be regulated. Preferably, it should be adjusted to pH 5 to 8, and, more preferably, to pH 6 to 7.

[0045] The aforementioned redox catalysts may be combinations of potassium persulfate, ammonium persulfate and acidic sodium sulfite and Rongalit, combinations of hydrogen peroxide and ascorbic acid and combinations of organic peroxides such as t-butyl hydroperoxide, benzoyl peroxide, cumene hydroperoxide and p-methane hydroperoxide with acid sodium sulfite and Rongalit. Combinations of organic peroxides and reducing agents are particularly desirable from the standpoint of executing polymerization in a stable manner. In addition, compounds containing divalent iron ions such as iron sulfate and chelating agents such as ethylenediaminetetraacetic acid disodium salt may be used in combination for the purpose of obtained stable catalytic activity.

[0046] The quantity of redox catalyst (initiator) that is used should be 0.01 to 10%, and, preferably, 0.05 to 5%, taking total monomer weight as the standard.

[0047] The concentration of solid matter in the emulsion of this invention should be 20 to 70%, and, preferably, 30 to 60%. When the concentration of solid matter exceeds 70%, the viscosity of the system is markedly increased, for which reason it is difficult to eliminate the heat that is generated accompanying the polymerization reaction and there is the drawback that a long time is required for extraction from the polymerization apparatus. When the concentration of solid matter is less than 20%, there are no problems from the standpoint of polymerization operations. However, only a small quantity of resin is produced in a single polymerization operation. When the economic factor is considered, this is markedly disadvantageous. Moreover, when the concentration is less than 20%, the paint film becomes thinner, performance is inferior and there are various problems affecting use such as disadvantages in painting workability.

[0048] The emulsion is comprised of microparticles having average particle diameters on the order of 0.02 to 0.7 μm . As a result, it has an excellent film forming capacity.

[0049] The proportion in which the emulsion (A) containing fluorine and the emulsion (B) containing alkoxysilyl groups is mixed (A/B, weight ratio) should be in the range of 10/90 to 90/10 as resin solid components. When it is outside this proportion, water resistance and long-term storage stability are decreased and a synergic effect cannot be obtained by mixing.

[0050] Crosslinking can be promoted by adding a hardener during painting of the composition of this invention. Organic metal compounds, acidic catalysts and basic catalysts can be used as hardeners. Organic aluminum compounds or organic tin compounds are particularly desirable from the standpoint of hardening activity. For example, they may be organic tin compounds such as dibutyl tin dilaurate, dibutyl tin dimaleate, dioctyl tin dimaleate, dibutyl tin dimethoxide, tributyl tin sulfite, dibutyl tin thioglycolate and tin octoate and organic aluminum compounds such as aluminum isopropylate, aluminum tris(acetylacetonate) and ethyl acetaldehyde aluminum diisopropylate,

[0051] These organic metal compounds are emulsified in advance with an emulsifying agent having an alkyl ether as its principal component and provide superior hardening activity and storage stability as a result of their addition at the time of use. The organic metal compound should be compounded in an amount of 0.1 to 10 parts (parts by weight; the same hereafter), and, preferably, of 0.1 to 5 parts, per 100 parts solid matter of the emulsion containing alkoxysilyl groups. When it is less than 0.01 parts, hardening activity is decreased. When it exceeds 10 parts, water resistance is decreased.

[0052] As required, additives that are used as components for ordinary paints, including pigments that are ordinarily used in paints (white pigments such as titanium dioxide, calcium carbonate, barium carbonate and kaolin), film making agents, colloidal silica, plasticizers, solvents, dispersants, thickeners, defoaming agents, preservatives and ultraviolet ray absorbents may be used in the hardenable composition that is obtained.

[0053] In addition, melamine resin and isocyanate compounds can be added as crosslinking agents. They can also promote rapid hardening.

[0054] The compositions of this invention can be used, for example, for inside and outside trimming and repair of buildings, on automobiles for clearing on metallic coatings, for direct coating of metals such as aluminum and stainless steel, for direct coatings on slate, concrete, tile, mortar, gypsum board, asbestos slate, asbestos board, precast concrete, light foam concrete, calcium silicate sheet and ceramic systems such as tile and brick, for coating of glass and stone materials and as top surface treatment agents. They can also be used as adhesive agents and pressure-sensitive adhesive agents.

[0055] They can also be blended with commercially sold aqueous paints. For example, when they are blended with thermosetting acrylic paints such as acrylic paints and acrylic melamine paints, alkyd paints, epoxy paints and fluorine resin paints, they can improve the weather resistance, acid resistance and solvent resistance of these paints.

[0056]

[Examples] We shall now describe this invention on the basis of examples. However, this invention is not limited by them.

[0057] Examples of Synthesis 1 (Synthesis of emulsion containing fluorine)

35 parts of ethyl vinyl ether, 2 parts of hydroxybutyl vinyl ether, 7 parts of the monomer having polyoxyethylene chains $\text{CH}_2=\text{CHO}(\text{CH}_2)_3(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, 120 parts of deionized water, 0.5 parts of ammonium salt of perfluorooctanoic acid, 0.5 parts of potassium carbonate, 0.03 parts of sodium hydrogensulfite and 0.14 parts of ammonium persulfate were introduced into an autoclave equipped with a stirrer and the mixture was subjected to bubbling with nitrogen gas for 1 hour, after which 56 parts of chlorotrifluoroethylene were introduced and a

reaction was carried out for 10 hours at 35°C. The concentration of the solid matter was adjusted to 40% with deionized water and emulsion A-1 containing fluorine being obtained.

[0058] Examples of Synthesis 2 and 3 (Synthesis of emulsions containing alkoxysilyl groups)

40 parts of deionized water, 0.35 parts of Rongalit, surfactants as shown in Table 1, 1.0 parts of polyoxyethylene nonylphenyl ether, 0.5 parts of ammonium acetate, 0.2 parts of t-butyl hydroperoxide and 20 parts of the 158 parts composition of the monomer emulsification solution of the composition shown in Table 1 were introduced as the initial charge into a reaction apparatus equipped with a stirrer, a reflux cooler, a nitrogen gas introduction tube and a dropping funnel. Next, the temperature was raised to 50°C and heating was carried out for 1 hour as nitrogen gas was being introduced, after which a mixture of 0.5 parts of t-butyl hydroperoxide and the remaining 138 parts of the aforementioned monomer emulsification solution were added dropwise over a 3 hour period. Following that, polymerization was carried out for 1 hour, the concentration of solid matter was adjusted to 40% using deionized water and emulsions B-1 and B-2 containing alkoxysilyl groups were obtained.

[0059]

[Table 1]

		Example of synthesis 2 (B-1)	Example of synthesis 3 (B-2)
Initially introduced activator (parts)	Dodecylbenzene sodium sulfonate	0.9	-
	Newcol-560SN *1	-	0.9
Composition of monomer emulsification solution (parts)	Butyl methacrylate	50	60
	Methyl methacrylate	20	20
	Butyl acrylate	25	13
	γ -Methacryloxypropyl trimethoxysilane	5	5
	MA-50 *2	-	2
	Deionized water	55	55
	Polyoxyethylene nonylphenyl ether	2	2
	Newcol-560SN *1	1.0	-
	Dodecylbenzene sodium sulfonate	-	1.0

*1 Anionic surfactant having polyoxyethylene chains (manufactured by Nippon Nyukazai, Ltd.)

*2 Methacrylic acid ester having polyoxyethylene chains (manufactured by Nippon Nyukazai, Ltd.)

[0060] Example 1 through 4 and Comparative Examples 1 and 2

The emulsions that were obtained were mixed in the proportions shown in Table 2 and the experiments indicated below were performed. The experimental results are also shown in Table 2.

[0061] (1) Long-term storage stability (external appearance characteristics)

The emulsions were stored for 1 month at 50°C and the state of the solution (external appearance characteristics) was observed visually.

[0062] (2) Long-term storage stability (5°C film forming capacity)

10 parts of CS12 (auxiliary film forming agent manufactured by Chisso, Ltd.) was added per 100 parts of solid matter in each emulsion that had been stored for 1 month at 50°C and the materials were allowed to stand overnight. They were then applied to glass plates, the glass plates to which they had been applied were allowed to stand overnight at 5°C and the states of their surfaces were observed. Cases in which there were no abnormalities were indicated by O, cases in which there were cracks in some places were indicated by Δ and cases in which there were cracks over the entire surface were indicated by X.

[0063] (3) Mechanical stability

Tests were conducted in accordance with JIS K 6392 for 5 minutes at a load of 15 kg using a Maron [phonetic] testing machine. After the test, the weight of the aggregated matter was measured and stability was expressed by the proportion (ppm) relative to the amount of solid matter in the charged emulsion.

[0064] (4) Water resistance

2 parts of dibutyl tin laurate was added to and mixed per 100 parts of solid matter of the emulsion and this mixture was applied to polyethylene sheet. The sheet was dried for 10 days at normal temperature, after which it was immersed in water for 1 day at normal temperature. The added weight was indicated as the proportion (%) relative to the weight of the film before immersion.

[0065]

[Table 2]

			Examples				Comparative Examples	
			1	2	3	4	1	2
Emulsion containing Fluorine (parts)		A-1	-	50	70	30	-	-
		Commercial product (40%) *1	50	-	-	-	100	-
Emulsion containing Alkoxysilyl groups (parts)		B-1	50	-	30	-	-	100
		B-2	-	50	-	70	-	-
Evaluation	Long-term Storage Stability	External appearance	no change	no change	no change	no change	no change	no change
		5°C film forming capacity	O	O	O	O	Δ	X
	Mechanical stability (ppm)		120	45	80	60	700	1600
	Water resistance (%)		6	8	10	7	25	15

*1 Fluoroolefin/vinyl ether copolymer type

[0066]

[Effect of the invention] The composition for aqueous paints of this invention is superior in respect to water resistance, durability, stability after long-term storage and film forming capacity.